

DERWENT-ACC-NO: 2000-587167

DERWENT-WEEK: 200063

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TITLE: Articles for forming films and sheets for packaging food
and medical products comprise multipolymer of
acrylonitrile and olefinically unsaturated monomer(s)
that is melt-processable in absence of solvent and water

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PATENT-ASSIGNEE: STANDARD OIL CO OHIO[STAH]

PRIORITY-DATA: 1999US-0255097 (February 22, 1999)

PATENT-FAMILY:

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LV MA MD MG MK MN MW MX NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR TT TZ UA
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APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
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B29D007/01, C08F220/44

ABSTRACTED-PUB-NO: WO 200050481A

BASIC-ABSTRACT:

NOVELTY - An article comprises a multipolymer of acrylonitrile and olefinically unsaturated monomer(s) that is melt-processable in the absence of solvent and water.

DETAILED DESCRIPTION - An INDEPENDENT CLAIM is also included for the production of high nitrile polymeric articles which involves thermal melt processing of the prepared multipolymer of acrylonitrile and olefinically unsaturated monomers in the absence of solvent and water by compression molding, continuous extrusion, injection/extrusion molding, blow molding, calendering, thermoforming and/or fusion coating at a temperature higher than the glass transition temperature of multipolymer to about 300 deg. C.

USE - For forming high nitrile articles such as films, sheets, pipes, gutters, siding, beams, buttons, rods, trays, containers, panels, jars, membranes, pellets, drums, carbon foils, coated laminates, wire coverings, substrates for

xerography, packaging, tapes, bottles, coatings, laminates, barrier products, membranes and/or molded articles (all claimed), for use in packaging food and medical products, barrier applications, electrical insulators, photographic and engineering films.

ADVANTAGE - The articles have dimensional stability, improved orientation, uniformity, strength, toughness, flexibility, resistance to degradation by UV light and biological attack and is free of voids.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: ARTICLE FORMING FILM SHEET PACKAGE FOOD MEDICAL PRODUCT COMPRISE
ACRYLONITRILE OLEFINIC UNSATURATED MONOMER MELT PROCESS ABSENCE
SOLVENT WATER

DERWENT-CLASS: A18 A92

CPI-CODES: A04-D03; A11-B01; A12-P01;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0260*R G0022 D01 D12 D10 D26 D51 D53 ; S9999
S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999 S1434 ; S9999
S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547 S1536 ; P0088

Polymer Index [1.2]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00642 G0340 G0339 G0260 G0022 D01 D11 D10 D12
D26 D51 D53 D58 D63 D84 F41 F89 ; S9999 S1285*R ; S9999 S1650 S1649
; S9999 S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ;
S9999 S1387 ; S9999 S1547 S1536 ; P0088

Polymer Index [1.3]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R01126 G0340 G0339 G0260 G0022 D01 D11 D10 D12
D26 D51 D53 D58 D63 D85 F41 F89 ; S9999 S1285*R ; S9999 S1650 S1649
; S9999 S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ;
S9999 S1387 ; S9999 S1547 S1536 ; P0088

Polymer Index [1.4]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00479 G0384 G0339 G0260 G0022 D01 D11 D10 D12
D26 D51 D53 D58 D63 D85 F41 F89 ; S9999 S1285*R ; S9999 S1650 S1649
; S9999 S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ;
S9999 S1387 ; S9999 S1547 S1536 ; P0088

Polymer Index [1.5]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00835 G0566 G0022 D01 D11 D10 D12 D51 D53 D58
D63 D84 F41 F89 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581
; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ;
S9999 S1547 S1536 ; P0088

Polymer Index [1.6]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00338 G0544 G0022 D01 D12 D10 D51 D53 D58 D69
D82 Cl 7A ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999
S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547
S1536 ; P1796 ; P0088 ; P0204

Polymer Index [1.7]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R01404 G0544 G0022 D01 D12 D10 D51 D53 D58 D69
D82 Br 7A ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999

S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547
S1536 ; P0088

Polymer Index [1.8]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00360 G0555 G0022 D01 D12 D10 D51 D53 D58 D69
D82 Cl 7A ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999
S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547
S1536 ; P0088 ; P0215

Polymer Index [1.9]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00708 G0102 G0022 D01 D02 D12 D10 D19 D18 D31
D51 D53 D58 D76 D88 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999
S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387
; S9999 S1547 S1536 ; P1741 ; P0088 ; P0157

Polymer Index [1.10]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00654 G0760 G0022 D01 D12 D10 D51 D53 D58 D60
D85 F37 F35 E00 E03 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999
S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387
; S9999 S1547 S1536 ; P0088

Polymer Index [1.11]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00966 G0055 G0044 G0033 G0022 D01 D02 D12 D10
D51 D53 D58 D84 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581
; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ;
S9999 S1547 S1536 ; P1150 ; P0088

Polymer Index [1.12]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00964 G0044 G0033 G0022 D01 D02 D12 D10 D51 D53
D58 D83 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999
S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547
S1536 ; P1150 ; P0088

Polymer Index [1.13]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00326 G0044 G0033 G0022 D01 D02 D12 D10 D51 D53
D58 D82 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999
S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547
S1536 ; P1150 ; P0088

Polymer Index [1.14]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0566*R G0022 D01 D12 D10 D51 D53 D58 D63 F41
F89 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999 S1434
; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547 S1536
; P0088

Polymer Index [1.15]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0588*R G0022 D01 D12 D10 D51 D53 D58 F34 ; S9999
S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999 S1434 ; S9999
S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547 S1536 ; P0088

Polymer Index [1.16]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0022*R D01 D51 D53 D12 D10 D58 F70*R ; S9999
S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999 S1434 ; S9999
S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547 S1536 ; P0088

Polymer Index [1.17]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0679*R G0022 D01 D51 D53 F23 D12 D10 D58 ; S9999
S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999 S1434 ; S9999
S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547 S1536 ; P0088

Polymer Index [1.18]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0102*R G0022 D01 D12 D10 D18 D51 D53 D19 D76
D58 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999 S1434
; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547 S1536
; P1741 ; P0088

Polymer Index [1.19]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0022*R D01 D51 D53 7A*R ; S9999 S1285*R ; S9999
S1650 S1649 ; S9999 S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999
S1569 ; S9999 S1387 ; S9999 S1547 S1536 ; P0088

Polymer Index [1.20]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0022*R D01 D51 D53 D60 ; S9999 S1285*R ; S9999
S1650 S1649 ; S9999 S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999
S1569 ; S9999 S1387 ; S9999 S1547 S1536 ; P0088

Polymer Index [1.21]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R24011 G0022 D01 D12 D10 D51 D53 D58 D60 D82 F62
; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999 S1434
; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547 S1536
; P0088

Polymer Index [1.22]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0022*R D01 D51 D53 D67 ; S9999 S1285*R ; S9999
S1650 S1649 ; S9999 S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999
S1569 ; S9999 S1387 ; S9999 S1547 S1536 ; P0088

Polymer Index [1.23]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0033*R G0022 D01 D02 D51 D53 ; S9999 S1285*R
; S9999 S1650 S1649 ; S9999 S1581 ; S9999 S1434 ; S9999 S1296 S1285
; S9999 S1569 ; S9999 S1387 ; S9999 S1547 S1536 ; P1150 ; P0088

Polymer Index [1.24]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0191 G0102 G0022 D01 D12 D10 D19 D18 D31 D51
D53 D58 D60 D76 D88 F62 Na 1A ; S9999 S1285*R ; S9999 S1650 S1649
; S9999 S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ;
S9999 S1387 ; S9999 S1547 S1536 ; P1741 ; P0088

Polymer Index [1.25]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0806 G0022 D01 D51 D53 Na 1A D61*R D12 D10 D58
D82 F62 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999
S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547
S1536 ; P0088

Polymer Index [1.26]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G4002 G0191 G0102 G0022 D01 D10 D12 D18 D19 D31
D51 D53 D58 D60 D76 D88 F62 ; S9999 S1285*R ; S9999 S1650 S1649
; S9999 S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ;
S9999 S1387 ; S9999 S1547 S1536 ; P1741 ; P0088

Polymer Index [1.27]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0453*R G0260 G0022 D01 D12 D10 D26 D51 D53 F70
F93 D58 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999
S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547
S1536 ; P0088

Polymer Index [1.28]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00444 G0453 G0260 G0022 D01 D12 D10 D26 D51 D53

D58 D83 F70 F93 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581
; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ;
S9999 S1547 S1536 ; P0088

Polymer Index [1.29]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00459 G0453 G0260 G0022 D01 D12 D10 D26 D51 D53
D58 D84 F70 F93 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581
; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ;
S9999 S1547 S1536 ; P0088

Polymer Index [1.30]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0760*R G0022 D01 D51 D53 E00 E01 D12 D10 D59
; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581 ; S9999 S1434
; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ; S9999 S1547 S1536
; P0088

Polymer Index [1.31]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; R00901 G0760 G0022 D01 D12 D10 D51 D53 D59 D60
D84 F37 F35 E00 E01 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999
S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387
; S9999 S1547 S1536 ; P0088

Polymer Index [1.32]

018 ; H0022 H0011 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D83 F12 ; G0748 G0715 G0022 D01 D12 D10 D51 D53 D58 D61*R
Na 1A F62 D84 ; S9999 S1285*R ; S9999 S1650 S1649 ; S9999 S1581
; S9999 S1434 ; S9999 S1296 S1285 ; S9999 S1569 ; S9999 S1387 ;
S9999 S1547 S1536 ; P0088

Polymer Index [1.33]

018 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51 D53 D58 D83 F12
; G0260*R G0022 D01 D12 D10 D26 D51 D53 ; R00642 G0340 G0339 G0260
G0022 D01 D11 D10 D12 D26 D51 D53 D58 D63 D84 F41 F89 ; R01126 G0340
G0339 G0260 G0022 D01 D11 D10 D12 D26 D51 D53 D58 D63 D85 F41 F89
; R00479 G0384 G0339 G0260 G0022 D01 D11 D10 D12 D26 D51 D53 D58
D63 D85 F41 F89 ; R00835 G0566 G0022 D01 D11 D10 D12 D51 D53 D58
D63 D84 F41 F89 ; R00338 G0544 G0022 D01 D12 D10 D51 D53 D58 D69
D82 Cl 7A ; R01404 G0544 G0022 D01 D12 D10 D51 D53 D58 D69 D82 Br
7A ; R00360 G0555 G0022 D01 D12 D10 D51 D53 D58 D69 D82 Cl 7A ;
R00708 G0102 G0022 D01 D02 D12 D10 D19 D18 D31 D51 D53 D58 D76 D88
; R00654 G0760 G0022 D01 D12 D10 D51 D53 D58 D60 D85 F37 F35 E00
E03 ; R00966 G0055 G0044 G0033 G0022 D01 D02 D12 D10 D51 D53 D58
D84 ; R00964 G0044 G0033 G0022 D01 D02 D12 D10 D51 D53 D58 D83 ;
R00326 G0044 G0033 G0022 D01 D02 D12 D10 D51 D53 D58 D82 ; G0566*R
G0022 D01 D12 D10 D51 D53 D58 D63 F41 F89 ; G0588*R G0022 D01 D12
D10 D51 D53 D58 F34 ; G0022*R D01 D51 D53 D12 D10 D58 F70*R ; G0679*R
G0022 D01 D51 D53 F23 D12 D10 D58 ; G0102*R G0022 D01 D12 D10 D18
D51 D53 D19 D76 D58 ; G0022*R D01 D51 D53 7A*R ; G0022*R D01 D51
D53 D60 ; R24011 G0022 D01 D12 D10 D51 D53 D58 D60 D82 F62 ; G0022*R
D01 D51 D53 D67 ; G0033*R G0022 D01 D02 D51 D53 ; G0191 G0102 G0022
D01 D12 D10 D19 D18 D31 D51 D53 D58 D60 D76 D88 F62 Na 1A ; G0806
G0022 D01 D51 D53 Na 1A D61*R D12 D10 D58 D82 F62 ; G4002 G0191
G0102 G0022 D01 D10 D12 D18 D19 D31 D51 D53 D58 D60 D76 D88 F62
; G0453*R G0260 G0022 D01 D12 D10 D26 D51 D53 F70 F93 D58 ; R00444
G0453 G0260 G0022 D01 D12 D10 D26 D51 D53 D58 D83 F70 F93 ; R00459
G0453 G0260 G0022 D01 D12 D10 D26 D51 D53 D58 D84 F70 F93 ; G0760*R
G0022 D01 D51 D53 E00 E01 D12 D10 D59 ; R00901 G0760 G0022 D01 D12
D10 D51 D53 D59 D60 D84 F37 F35 E00 E01 ; G0748 G0715 G0022 D01
D12 D10 D51 D53 D58 D61*R Na 1A F62 D84 ; S9999 S1285*R ; S9999
S1650 S1649 ; S9999 S1581 ; S9999 S1434 ; S9999 S1296 S1285 ; S9999
S1569 ; S9999 S1387 ; S9999 S1547 S1536 ; H0033 H0011 ; P1150 ;

P1741 ; P1796 ; P0088 ; P1876

Polymer Index [1.34]

018 ; ND04 ; B9999 B3623 B3554 ; N9999 N6940 N6939 ; B9999 B5618
B5572 ; N9999 N6462 N6440 ; N9999 N6484*R N6440 ; N9999 N5970*R
; K9392 ; N9999 N6177*R ; N9999 N7147 N7034 N7023 ; N9999 N6451
N6440 ; N9999 N6111 N6097 ; Q9999 Q7818*R ; Q9999 Q6859 Q6826 ;
Q9999 Q8731 Q8719 ; Q9999 Q8399*R Q8366 ; Q9999 Q8435 Q8399 Q8366
; N9999 N5878 ; K9676*R ; K9483*R ; B9999 B5163 B5152 B4740 ; B9999
B5174 B5152 B4740 ; Q9999 Q8060 ; K9621*R ; N9999 N7192 N7023 ;
N9999 N5914*R ; Q9999 Q7556 ; Q9999 Q8366*R ; Q9999 Q8571 Q8366
; K9596 K9483 ; K9712 K9676 ; Q9999 Q6780 ; Q9999 Q8617*R Q8606
; Q9999 Q8662 Q8606 ; Q9999 Q8935*R Q8924 Q8855 ; ND01 ; ND10 ;
Q9999 Q7589*R ; B9999 B3758*R B3747 ; B9999 B4193 B4091 B3838 B3747
; B9999 B4091*R B3838 B3747 ; B9999 B4035 B3930 B3838 B3747 ; B9999
B4615 B4568 K9847 ; K9869 K9847 K9790 ; B9999 B4579 B4568 ; B9999
B5094 B4977 B4740 ; B9999 B4148 B4091 B3838 B3747 ; B9999 B4046
B3930 B3838 B3747 ; B9999 B4159 B4091 B3838 B3747 ; B9999 B4568*R
; B9999 B4295 B4240 ; K9438 ; B9999 B5414*R B5403 B5276 ; ND07

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(21) International Application Number: PCT/US00/02624 (22) International Filing Date: 2 February 2000 (02.02.00) (30) Priority Data: 09/255,097 22 February 1999 (22.02.99) US (71) Applicant: THE STANDARD OIL COMPANY [US/US]; Law Dept. – MC 1907A, 200 East Randolph Drive, Chicago, IL 60601 (US). (72) Inventors: PERCEC, Elena, Simona; Locust on the Park, 201 South 25th Street, Philadelphia, PA 19103 (US). BALL, Lawrence, E.; 4288 West Bath Road, Akron, OH 44333 (US). JORKASKY, Richard, J.; 6060 Stow Road, Hudson, OH 44236 (US). (74) Agent: DISALVO, Joseph; BP Amoco Corporation, Law Dept. – MC 1907A, 200 East Randolph Drive, Chicago, IL 60601 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: THERMALLY MELT PROCESSABLE MULTIPOLYMERS OF ACRYLONITRILE AND OLEFINICALLY UNSATURATED MONOMERS (57) Abstract <p>An enormous array of acrylic articles can be prepared from a high nitrile multipolymer that can be melt processed in the absence of solvent and water by continuous extrusion, compression molding, injection/extrusion molding, blow molding, calendering, thermoforming, fusion coating and the like.</p>		

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AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
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BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
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BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
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ER	Estonia						

The present invention relates to the thermal melt processability of
5 multipolymers of acrylonitrile and olefinically unsaturated monomers. A unique
combination of acrylonitrile monomer with an olefinically unsaturated monomer(s)
provides for high nitrile multipolymers that are thermally melt processed into superior
articles.

It is understood that the term "acrylic" herein means multipolymers comprising at least 85% by weight acrylonitrile units. It is understood that the terms "multipolymer", "multipolymers" and "multipolymer of acrylonitrile monomer and olefinically unsaturated monomers" herein includes co-polymers, terpolymers and multipolymers throughout the specification.

The known processes for the manufacture of articles produced from acrylic polymers are based on solvent technology. Acrylic polymers in general cannot be processed in the melt, for example by melt spinning or melt extruding, since the decomposition temperature of the acrylic polymer lies below the temperature at which it melts. Acrylic polymers containing plasticizers and/or solvents have a melting point sufficiently low as to allow processing without excessive decomposition. Acrylic articles produced by these various processing methods usually contain residual solvent or plasticizer. The acrylic article is generally freed of such substances by washing and drying processes.

25 The production of acrylic materials from solution-based extrusion is undesirable due to the problems of solvent removal. The removal of solvent from the material is not always complete, or uniform, resulting in voids and lack of homogeneity in the structure of the acrylic material.

Acrylic polymer products prepared by the prior art techniques have substantial
30 voids that diminish the mechanical properties of the products. The manufacture of
acrylic products with satisfactory properties has in the past proved to be particularly
difficult. This is in contrast to other polymeric materials, such as polyolefins,

polyesters, and polyamides, where solvent-free melt processing techniques for the manufacture of the products can be applied.

It is advantageous to produce high nitrile materials including acrylics by a waterless, solventless process employing a melt processable high nitrile multipolymer. It is further desirable to produce materials from melt processable high nitrile multipolymers because the resulting materials are homogeneous throughout and substantially void-free. Furthermore, it is advantageous to produce high nitrile multipolymer materials from a melt process and not from a solvent process because there is no solvent to be removed and recovered.

Summary of the Invention

It has been discovered that articles can be obtained from a melt processable, solventless, waterless multipolymer of acrylonitrile and olefinically unsaturated monomers. In the instant invention, a process for the production of high nitrile polymeric materials comprises: (a) preparing a melt processable multipolymer of acrylonitrile and olefinically unsaturated monomers, (b) thermal melt processing of the multipolymer of acrylonitrile and olefinically unsaturated monomers in the absence of solvent and water at a temperature higher than the glass transition temperature of the multipolymer to about 300°C, wherein such thermal melt processing steps are selected from the group consisting of (i) compression molding, (ii) continuous extrusion, (iii) injection/extrusion molding, (iv) blow molding, (v) calendering, (vi) thermoforming, (vii) fusion coating and the like.

The present invention provides for superior articles which are homogeneous and have a high degree of orientation due to the uniqueness of the multipolymers of the acrylonitrile monomer and olefinically unsaturated monomers that are thermally melt processable.

Description of the Invention

In accordance with the present invention, articles are produced from a novel solventless, waterless, melt processable multipolymer of acrylonitrile monomer and olefinically unsaturated monomers. Further, in accordance with the present invention, a method provides for a homogenous and substantially uniform multipolymer of acrylonitrile monomer and olefinically unsaturated monomers that is melt processed

in the absence of solvent and water, at a temperature higher than the glass transition temperature of the multipolymer to about 300°C, wherein such multipolymer is melt processed by a method selected from the group consisting of compression molding, extrusion by continuous or injection method, blow molding, calendering, thermoforming, fusion coating, and the like.

The unique melt processable multipolymer used in this invention comprises acrylonitrile monomer and olefinically unsaturated monomers, wherein the high nitrile multipolymer is homogeneous with a substantially uniform microstructure and can be obtained according to USPN 5,618,901 entitled "A Process For Making A High Nitrile MultiPolymer Prepared From Acrylonitrile and Olefinically Unsaturated Monomers"; USPN 5,602,222 entitled "A Process For Making An Acrylonitrile Methacrylonitrile Olefinically Unsaturated Monomers"; and USPN 5,596,058 entitled "Process for Making Acrylonitrile/Methacrylonitrile Co-polymers," all incorporated herein.

The high nitrile multipolymer comprises about 50% to about 99%, preferably about 76% to about 98%, more preferably about 80% to about 95% and most preferably about 85% to about 92% of polymerized acrylonitrile monomer and at least one of about 1% to about 50%, preferably about 2% to about 24%, more preferably about 5% to 20% and most preferably 8% to about 15% polymerized olefinically unsaturated monomer.

It will be readily apparent to one skilled in the art that the high nitrile multipolymer may be further modified by the addition of processing agents, dyes, leaching agents, pigments, delustering agents, lustering agents, stabilizers, static control agents, antioxidants, reinforcing agents, fillers and the like. It is understood that any additive possessing the ability to function in such a manner can be used as long as it does not have a deleterious effect on the melt and/or thermal characteristics of the high nitrile multipolymer or products thereof.

The olefinically unsaturated monomer(s) is employed in the high nitrile multipolymer is one or more of an olefinically unsaturated monomer with a C=C double bond polymerizable with acrylonitrile. The olefinically unsaturated monomer employed in the multimonomer mixture can be a single polymerizable monomer or a combination of polymerizable monomers. The choice of olefinically unsaturated

monomer or combination of monomers depends on the properties desired to impart to the resulting high nitrile multipolymer product.

The olefinically unsaturated monomer(s) includes but is not limited to acrylates, methacrylates, acrylamide and its derivatives, methacrylamide and its derivatives, maleic acid and derivatives, vinyl esters, vinyl ethers, vinyl amides, vinyl
5 ketones, styrenes, halogen containing monomers, ionic monomers, acid containing monomers, base containing monomers, olefins and the like.

The acrylates include but are not limited to C₁ to C₁₂ alkyl, aryl and cyclic acrylates; such as methyl acrylate, ethyl acrylate and functional derivatives of the
10 acrylates such as 2-hydroxyethyl acrylate, 2-chloroethyl acrylate and the like. The preferred acrylates are methyl acrylate and ethyl acrylate.

The methacrylates include but are not limited to C₁ to C₁₂ alkyl, aryl and cyclic methacrylates; such as methyl methacrylate, ethyl methacrylate, phenyl methacrylate, butyl methacrylate, isobornyl methacrylate, 2-ethylhexyl methacrylate
15 and functional derivatives of the methacrylates such as 2-hydroxyethyl methacrylate, 2-chloroethyl methacrylate and the like.

The preferred methacrylate is methyl methacrylate.

The acrylamides and methacrylamides and each of their N-substituted alkyl and aryl derivatives include but are not limited to acrylamide, methacrylamide,
20 N-methyl acrylamide, N, N-dimethyl acrylamide and the like.

The maleic acid monomers include but are not limited to maleic acid monododecyl maleate, didodecyl maleate, maleimide, N-phenyl maleimide.

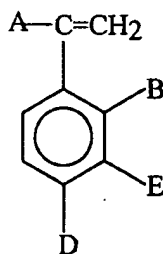
The vinyl ethers include but are not limited to C₁ to C₈ vinyl ethers such as ethyl vinyl ether, butyl vinyl ether and the like.

25 The vinyl esters include but are not limited to vinyl acetate, propionate, butyrate and the like. The preferred vinyl ester is vinyl acetate.

The vinyl amides include but are not limited to vinyl pyrrolidone and the like.

The vinyl ketones include but are not limited to C₁ to C₈ vinyl ketones such as ethyl vinyl ketone, butyl vinyl ketone and the like.

30 The styrenes include but are not limited to substituted styrenes, multiple-substituted styrenes, methylstyrenes, styrene, indene and the like. Styrene is of the formula:



wherein each of A, B, D and E is independently selected from hydrogen (H), C₁ to C₄
 5 alkyl groups and halogen.

The halogen containing monomers include but are not limited to vinyl chloride, vinyl bromide, vinyl fluoride, vinylidene chloride, vinylidene bromide, vinylidene fluoride, halogen substituted propylene monomers and the like. The preferred halogen containing monomers are vinyl chloride, vinyl bromide and vinylidene
 10 chloride.

The ionic monomers include but are not limited to sodium vinyl sulfonate, sodium styrene sulfonate, sodium methallyl sulfonate, sodium acrylate, sodium methacrylate and the like. The preferred ionic monomers are sodium vinyl sulfonate, sodium styrene sulfonate and sodium methallyl sulfonate.

15 The acid containing monomers include but are not limited to acrylic acid, methacrylic acid, vinyl sulfonic acid, itaconic acid, styrene sulfonic acid and the like. The preferred acid containing monomers are itaconic acid, styrene sulfonic acid and vinyl sulfonic acid.

The base containing monomers include but are not limited to vinyl pyridine,
 20 2-aminoethyl-N-acrylamide, 3-aminopropyl-N-acrylamide, 2-aminoethyl acrylate, 2-aminoethyl methacrylate and the like.

The olefins include but are not limited to isoprene, butadiene, C₂ to C₈ straight chained and branched alpha-olefins such as propylene, ethylene, isobutylene, 1-butene and the like.

25 The preferred multipolymer includes but is not limited to an acrylonitrile monomer polymerized with at least one monomer of methyl acrylate, ethyl acrylate, vinyl acetate, methyl methacrylate, vinyl chloride, vinyl bromide, vinylidene chloride, sodium vinyl sulfonate, sodium styrene sulfonate, sodium methallyl sulfonate,

itaconic acid, styrene, sulfonic acid, vinyl sulfonic acid, isobutylene, ethylene, propylene and the like.

The high nitrile multipolymer is thermally melt processed in the absence of solvent and water, and may then be compression molded from a powder, pellet, tablet or the like of the multipolymer. The multipolymer is placed in the mold cavity and exposed to sufficient heat to allow flow. The mold is under pressure generally in the range of about 10 psi to about 50,000 psi for a time period sufficient to achieve homogeneous molding. The temperature is higher than the glass transition temperature of the multipolymer to about 300°C, preferably about 130°C to about 280°C. Generally, the multipolymer is placed in the bottom half of a mold cavity mounted in a heated press. The press is closed, bringing the bottom half of the mold against the top half under pressure and multipolymer melts. After cooling, the press is opened and the multipolymer article has assumed the shape of the molded cavity. The shape of the article is determined by the shape of the mold. The surface of the molded article is determined by the surface of the mold.

The multipolymer articles that are formed by compression molding are films, sheets, tapes, membranes and laminates, and objects such as buttons, containers, trays and the like.

In another embodiment of the invention, the high nitrile multipolymer is calendered. Calendering is melting the multipolymer between successive pairs of co-rotating parallel rolls to form a film or a sheet. The general process considerations are the temperature, roll speed, finish, gauge, orientation and embossing. The process temperature is sufficient to achieve melt flow and this temperature is higher than the glass transition temperature of the multipolymer to about 300°C, preferably about 130°C to about 280°C. The thickness of the film or sheet is dependent upon the roll clearance. The surface of the finished film or sheet is dependent on the finish on the rolls. The multipolymer articles that are formed by calendering are high nitrile polymeric films, sheets, tapes, laminates and the like.

In another embodiment of the invention, the high nitrile multipolymer is continuously melt-extruded. The multipolymer is placed in an extruder as a powder, pellet, tablet or the like. The temperature is sufficient to achieve melt flow, and is at a

temperature higher than the glass transition temperature of the high nitrile multipolymer to about 300°C, preferably about 130°C to about 280°C.

Generally, the extruder incorporates one or more screw(s) rotating in a cylindrical barrel with an entry port mounted at the feed end and a shaped die mounted at the discharge end. The high nitrile multipolymer enters a heated environment, where it is melted, mixed and conveyed through the die by the screw(s). The temperature is such that the high nitrile multipolymer is exposed to a temperature higher than the glass transition temperature of the multipolymer to about 300°C, preferably about 130°C to about 280°C.

In continuous extrusion, the desired article is defined by the extrudate shape which is dependent upon the die used. A slit die is used to produce high nitrile polymeric sheets, films, tapes, membranes, laminates and the like. A shaped die is used to produce high nitrile polymeric articles such as pipes, beams, gutters, siding, rods, pellets cut from a rod, and the like.

An alternative extrusion method is injection/extrusion molding where the screw acts as a ram or plunger to inject the melted multipolymer into the mold. The temperature is such that the high nitrile multipolymer is exposed to a temperature higher than the glass transition temperature of the multipolymer to about 300°C, preferably about 130°C to about 280°C. When the high nitrile multipolymer is sufficiently solidified, the mold halves separate and the article is ejected.

In another embodiment of the invention, the high nitrile multipolymer is blow molded. Blow molding is a form of injection molding used to make hollow articles such as bottles and the like. The high nitrile multipolymer is melted at a temperature higher than the glass transition temperature of the multipolymer to about 300°C, preferably 130°C to about 280°C and is extruded as a tube-like parison into an open mold. The mold is then closed around the tube, parison or ring die, and the end of the tube is pinched together by the mold. Air pressure is fed through the die into the tube, which expands to fill the mold, and the part is cooled and then ejected.

In another embodiment of the invention, the high nitrile multipolymer is thermoformed. The high nitrile multipolymer sheet(s) is thermoformed into a desired shape. Thermoforming includes vacuum forming, drape forming, pressure forming and matched-mold forming. The central element of a thermoforming system is the

tooling, comprising the mold and a means to trim. In a thermoforming process, the high nitrile multipolymer sheet is thermally softened, and then using a mold, it is formed into the desired shape. The general technique consists of clamping, heating, forming and trimming. The temperature is higher than the glass transition
5 temperature of the high nitrile multipolymer sheet to about 300°C, preferably about 130°C to about 280°C. In thermoforming male, female and matched male/female molds can be used. An auxiliary operation is prestretching the hot sheet to control the thickness of the final product. Thermoforming is a process for converting a sheet into an article such as a sign, a tray for packaging and the like.

10 Another embodiment of the invention is fusion coating. In fusion coating, the high nitrile multipolymer is used to either to coat various articles (powder coating) or obtain articles by fusion molding (rotational molding). Methods to make articles by a fusion coating process include, but are not limited to, fluidized bed, electrostatic spray, electrostatic fluidized bed, plasma spray and the like. The high nitrile
15 multipolymer powder is usually dispersed in air and sprayed or blown onto a preheated mold or article to be coated, where the multipolymer melts and forms a coating on the mold or article. The high nitrile multipolymer is fusion coated at a temperature in the range of the glass transition temperature of the multipolymer to about 300°C, preferably about 130°C to about 280°C. The coated article is then
20 cooled and packaged.

An alternative fusion coating process is rotational molding. Generally, in rotomolding operations, the mold or cavity is filled with a certain amount of powder, the mold halves are closed, placed in a heated oven, and the mold is rotated biaxially. During heating, the multipolymer melts, fuses, and densifies into the shape
25 of the mold or cavity. The high nitrile multipolymer is fusion coated at a temperature in the range of the glass transition temperature of the multipolymer to about 300°C, preferably about 130°C to about 280°C. The mold is cooled, opened and the finished article is removed.

In all embodiments of the invention, the high nitrile multipolymer is thermally
30 melt processed in the absence of solvent and water. The multipolymer can be processed with small amounts of stabilizer and processing aids so long as it does not

have a deleterious effect on the melt and/or thermal characteristics of the multipolymer and/or article.

In all the embodiments, the articles can be further processed by a combination of any or all of the thermoforming methods. Such processing steps include, but are not limited to orientation, blowing, thermoforming, lamination, coating, extrusion, sealing, prestretching and the like. Such articles include components stretched uniaxially and/or biaxially films, sheets, tapes, laminates, coated structures, composite structures and the like.

The high nitrile multipolymer is unique because it is melt processed in the absence of solvent and water. The olefinically unsaturated monomers are uniformly interdispersed among the acrylonitrile units in the multipolymer. This dispersion of the co-monomers uniformly along the polymer chain reduces the length of the acrylonitrile monomer sequences. These shorter acrylonitrile sequenced multipolymers have a lower melting point and reduced melt viscosity which allows melt processing. The high nitrile multipolymer allows for unique properties in the articles such as dimensional stability, improved orientation, substantially free of voids, uniformity, strength, toughness, flexibility, resistance to degradation by UV light, resistance to biological attack and the like.

This invention allows for the high nitrile articles to be formed into films, sheets, pipes, carbon foils, coated laminates, wire coverings, substrates for xerography, packagings, tapes, bottles, coatings, laminates, barrier products, membranes, molded articles and the like. The products of this invention may be further used in packaging food and medical products, barrier applications, electrical insulators, photographic films, engineering films and the like.

Examples

The following examples are presented to illustrate the present invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples.

Example 1

Preparation of the High Nitrile Multipolymer

A multipolymer containing 85/15 acrylonitrile/methyl acrylate was prepared. A
5 50-gallon, stainless steel, circulating hot water jacketed reactor was equipped with a
reflux condenser, a thermocouple/controller, a turbin for agitation, which was set at
about 150 to 250 rpm, a nitrogen purge, and a feed pump.

Multipolymer composition: The overall components for the polymerization
example were as follows:

10		<u>lbs.</u>
	Water	225
	Dowfax 8390 (35% active)	8.57
	Acrylonitrile (AN)	85
	Methyl Acrylate (MA)	15
15	n-Dodecyl Mercaptan	1.8
	Ammonium Persulfate	0.07

Dowfax is available from Dow Chemical Co.

Procedure: The reactor was pre-charged with water, 10% of the comonomers,
10% of the mercaptan, and the surfactant with stirring at about 150-250 rpm. The
20 reactor was heated to about 60°C under nitrogen purging. Ammonium persulfate was
added to the reactor to initiate the polymerization reaction. The remaining mixture of
multimonomers and mercaptan was continuously pumped into the reactor at a
constant rate over about four hours.

After the polymerization reaction was complete, the resulting multipolymer
25 latex was filtered through a cloth filter bag to collect and separate any coagulum from
the latex. The latex was coagulated in water in a countercurrent train of three
overflowing stirred tanks. These tanks were set at about 70-98°C and contained
about 1% to about 3% aluminum sulfate based on the polymer in the latex. The
washed multipolymer crumb was filtered and dried in a Fitzpatrick fluidized bed dryer
30 at about 70°C for about 3 hours. The multipolymer was then analyzed and
determined to be 85/15 acrylonitrile/methyl acrylate by NMR spectroscopy.

Example 2

Extrusion/Pelletization of the High Nitrile Multipolymer

The high nitrile multipolymer was prepared by the method described above and recovered as powder. The powder was extruded using a 1.25 inch Brabender
5 extruder (C. W. Brabender Instruments, Inc., S. Hackensack, NJ) having a general purpose screw of 30/1 L/D, a compression ratio of about 2.3 and fitted with a heated round die with a 3/16 inch nozzle. The four zone temperatures were set at temperatures about 180°C, about 180°C, about 180°C and about 180°C with a die temperature about 185°C to achieve consistent melting.

10 The uniformly melted, round extrudate rod was conveyed by an air cooled moving belt to a one horsepower, spinning knife chopper (Killion Extruders, Inc., Cedar Grove, NJ) wherein the cooled rod was cut into 1/8-1/4 inch pellets.

Example 3

15 High Nitrile Multipolymer Film by Blow Extrusion

The high nitrile multipolymer of AN/MA 85/15 with a molecular weight of about 60,000 was blown into biaxially oriented film on a film blowing line employing an extruder, ring die equipped with internal air blowing line, pinch rolls and take-up winder. A Killion, Inc. 3/4 inch extruder was employed which had 3 heating zones and
20 was equipped with a 2 heater blowing ring die (5 zones in all). The line was equipped with a variable air pressure and a crimping tower with wind-up. The ring die was 2 inches in diameter (6.28-inch circumference) with a die gap of 0.15 mil.

Multipolymer pellets were charged to the extruder and the molten resin was extruded through the ring die at melt temperatures from about 350°F to about 380°F.
25 Upon pinching the extruded tube and the application of internal air pressure, a stable bubble was achieved with about a 6 inch diameter. Simultaneously, the take-up speed was adjusted to provide machine direction drawing. The extrusion/blow operation produced a clear, colorless, shiny film with the following properties.

Composition 85/15	Bubble Diameter (inch)	Take-up setting*	Thickness (mil)	Overall Draw	Machine/ Transverse draw
AN/MA	6	6	1.7	5.6	1.9/3
AN/MA	6	9	1.5	10	3.3/3
AN/MA	6	7	1.8	8.3	2.8/3

*Speed control setting 1 to 10.

Example 4

5 High Nitrile Multipolymer Injection Molding

Multipolymers having the following characteristics were prepared by the method and pelletization procedures as described above.

Composition	Comonomer Wt. Ratio	Molecular Weight (Mw)
AN/MA	76/24	90,000
AN/MA	85/15	90,000

- 10 These multipolymers were injection molded into physical test specimens on a Simutoyo 75 ton injection molding machine. The general purpose screw had a 24/1 4D and a 3:1 compression ratio with no mixing elements. The extruder of the injection molder had 5 zones set sequentially at about 420°F, about 435°F, about 450°F, about 450°F and about 450°F with a mold temperature of about 140°F.
- 15 The mold consisted of three ASTM test specimen shapes; a tensile bar (Type 1), a flexural bar (5 inch x 0.5 inch x 0.125 inch) and an impact/optical disc (2.4 inch d x 0.125 inch).

- Physical and optical properties were determined from the ASTM test specimens. The flexural, tensile and impact data were calculated according to
- 20 ASTMs D790, D638, D256. The optical data was obtained from a Hunterlab Ultrascan colorimeter (Hunter Associates Laboratories, Inc., Reston, Virginia).

Physical Properties

Composition	Flexural Strength	Flexural Modulus	Dart Impact Max Load	Daft Impact Total Energy	Tensile Strength
Units	psi	ksi	lb	ft-lb	psi
AN/MA 76/24	21	721	187	1.1	10952
AN/MA 85/15	22.5	669	241	1.5	10051

5

Optical Properties*

Composition	Yellowness Index	Haze (%)
AN/MA 76/24	64.5	35.7
AN/MA 85/15	39.9	33.7

* 0.125 inch specimens

The injection molded articles had good strength and good optical properties.

10

Example 5

High Nitrile Multipolymer Films by Compression Molding

- A. Pellets of a high nitrile multipolymer (AN/MA 85/15 with a molecular weight MW of 68,000) were transferred to a preheated mold in a preheated Wabash press. A plaque (97.5 cm x 15 x 0.31 cm) was prepared by pressing the mold at about 14.0 MPA at about 220°C for two minutes followed by cooling the press under the applied pressure for about 10-12 minutes. While the plaque was still hot (about 90°C), it was cut into 2.5 cm squares using a band saw. Films were prepared by compressing the molded 2.5 cm squares between top and bottom platens covered with EKCO Baker's cookie sheet (metallic surface coated with nontoxic FDA approved silicone compounds). Conditions were 7.2 MPA at about 225°C for one minute. The thickness of the films was about 8-9 mils.
- B. Films were also prepared in one step by preheating a 15-cm by 15-cm cookie sheet covered platen in a press that was preheated to about 230°C. About 20

g of the pellets of the high nitrile multipolymer were spread over the bottom cookie sheet platen. After the pellets were essentially melted, the top 15 cm x 15 cm cookie sheet platen was positioned over the bottom, and the assembly was pressed at about 230°C at a pressure of about 25,000 psi for about a minute and then cooled to room temperature.

- 5
- C. Films were also prepared in one step by placing the high nitrile multipolymer pellets into a stainless steel frame of the following dimensions 5 inch x 5 inch x 0.5 mm. Kapton film was used on both sides when the assembly was pressed at a pressure of about 25,000 psi at a temperature of about 230°C. This demonstrates the ease of preparation of high nitrile melt processable multipolymer films via compression molding.
- 10

Example 6

High Nitrile Multipolymer Sheets by Extrusion

- 15 Sheets were obtained by melt extrusion of a high nitrile multipolymer resin (AN/MA 85/15 with a molecular weight of about 90,000) using a 3/4-inch Brabender extruder L/D= 25/1) equipped with a slit die. The sheets were completely transparent and had a thickness of about 1mm and a width in the range of 60-80 mm. This demonstrates the ease of preparation of high nitrile processable multipolymer sheets via extrusion.
- 20

Example 7

Uniaxial Orientation of High Nitrile Multipolymer Sheets

- 25 Samples from Example 6 were uniaxially oriented by drawing the extruded sheets in one direction, allowing free contraction to occur in the direction perpendicular to the draw direction. The sheets were drawn in a hot air Sintech oven mounted in a tensile testing machine. Samples were initially set in clamps of the testing machine for about 3-5 minutes to achieve equilibrium temperature and then drawn at a cross head speed of about 5-50 mm/sec to the required draw ratio as is indicated in the table below.
- 30

Composition	Drawing	Preheating	Drawing Speed (mm/sec.)	Draw Ratio
	Temperature (°C)	Time (sec.)		
AN/MA 85/15	130	300	30	1.5
AN/MA 85/15	130	600	5	1.5
AN/MA 85/15	130	180	50	1.6

These examples demonstrate that sheets made from the high nitrile multipolymers are uniaxially drawn.

5

Example 8

Biaxial Orientation of High Nitrile Multipolymer Compression Molded Films

A film obtained by compression molding (from Example 5(C)) was biaxially drawn on a Iwamoto two-way stretch machine that allows simultaneous drawing along two perpendicular directions in a hot air oven. A draw ratio of 1.1 x 1.1 was achieved by using a drawing temperature of about 130°C and a drawing speed of about 50 mm/sec.

Polyethylene terephthalate (PET) tape was mounted around the high nitrile multipolymer film in order to avoid the exposure to higher temperatures of some high nitrile multipolymer film areas (which were in direct contact with the metal clamps used). In this case, a draw ratio of 1.4 x 1.4 was readily achieved.

These examples demonstrate that high nitrile multipolymers can be melt processed into films, sheets, rods, pellets, tapes and articles. They can also be treated, handled, and oriented uniaxially or biaxially as required in different applications.

From the above description of examples and invention, those skilled in the art will perceive improvements, changes and modifications in the invention. Such improvements, changes and modifications are intended to be covered by the claims.

What is claimed:

1. An article comprising a multipolymer of acrylonitrile and olefinically unsaturated monomer(s) wherein said multipolymer is melt processable in the absence of solvent and water.
- 5 2. The article of claim 1 wherein the high nitrile multipolymer comprises about 50% to about 99% acrylonitrile and at least one of about 1% to about 50% polymerized olefinically unsaturated monomer.
3. The article of claim 1 wherein the high nitrile multipolymer comprises about 76% to about 98% acrylonitrile and at least one of about 2% to about 24%
10 polymerized olefinically unsaturated monomer.
4. The article of claim 1 wherein the high nitrile multipolymer comprises about 80% to about 95% acrylonitrile and at least one of about 5% to about 20% polymerized olefinically unsaturated monomer.
5. The article of claim 1 wherein the high nitrile multipolymer comprises
15 about 85% to about 92% acrylonitrile and at least one of about 8% to about 15% polymerized olefinically unsaturated monomer.
6. The article of claim 1 wherein the olefinically unsaturated monomer is selected from the group consisting of acrylates, methacrylates, acrylamide and its derivatives, methacrylamide and its derivatives, maleic acid and its derivatives, vinyl
20 esters, vinyl ethers, vinyl amides, vinyl ketones, styrenes, halogen containing monomers, ionic monomers, acid containing monomers, base containing monomers, olefins and combinations thereof.
7. The article of claim 1 wherein the acrylonitrile monomer is polymerized with at least one monomer is selected from the group consisting of methyl acrylate,
25 ethyl acrylate, vinyl acetate, methyl methacrylate, vinyl chloride, vinyl bromide, vinylidene chloride, sodium vinyl sulfonate, sodium styrene sulfonate, sodium methallyl sulfonate, itaconic acid, styrene, sulfonic acid, vinyl sulfonic acid, isobutylene, ethylene, propylene and combinations thereof.
8. The process for the production of high nitrile polymeric articles
30 comprising:
 - (a) preparing a melt processable multipolymer of acrylonitrile and olefinically unsaturated monomers;

(b) thermal melt processing of the multipolymer of acrylonitrile and olefinically unsaturated monomers in the absence of solvent and water at a temperature higher than a glass transition temperature of the multipolymer to about 300°C wherein such thermal melt processing step is selected from the group consisting of (i) compression molding; (ii) continuous extrusion; (iii) injection/extrusion molding; (iv) blow molding; (v) calendering; (vi) thermoforming; (vii) fusion coating; and combinations thereof.

9. The process of claim 8 wherein the thermal melt processing temperature is in the range of about 130°C to about 280°C.

10. The process of claim 8 wherein the multipolymer articles formed by compression molding are selected from the group consisting of film, sheets, tapes, membranes, laminates and objects that are the shape of the mold and combinations thereof.

11. The process of claim 8 wherein the thermal melt processing step is calendering the multipolymer and wherein the articles formed are selected from the group consisting of high nitrile polymeric films, sheets, tapes, laminates, membranes and combinations thereof.

12. The process of claim 8 wherein the thermal melt processing step is extruding the multipolymer and wherein the articles formed are determined by the shape of the die and are selected from the group consisting of polymeric sheets, films, blown films, tapes, membranes, laminates, pipes, beams, gutters, siding, rods and combinations thereof.

13. The process of claim 8 wherein the thermal melt processing step is injection/extrusion molding of the multipolymer and wherein the articles produced are determined by the shape of the mold.

14. The process of claim 8 wherein the thermal melt processing step is blow molding the multipolymer and wherein the articles formed are hollow articles selected from the group consisting of bottles, drums, jars, containers and combinations thereof.

15. The process of claim 8 wherein the processing step is thermoforming a sheet of multipolymer into an article whose shape is determined by the mold.

16. The process of claim 8 wherein the thermal melt processing step is fusion coating the multipolymer which melts and forms a coating on the mold or article, resulting in a coated article.

17. The process of claim 8 wherein the thermal melt processing step is rotational fusion molding and wherein the resulting article is the shape of the mold.

18. The process of claim 8 wherein the high nitrile polymeric material is further processed after the thermal processing step by a process selected from the group consisting of orientation, blowing, thermoforming, lamination, coating, extrusion, sealing, prestretching and combinations thereof.

19. The process of claim 8 wherein the articles formed are selected from the group consisting of uniaxial films, biaxial films, blown films, sheets, tapes, laminates, membranes coated structures, composite structures and combinations thereof.

20. The process of claim 8 wherein the high nitrile articles are formed are selected from the group consisting of films, sheets, pipes, gutters, siding, beams, buttons, rods, trays, containers, panels, jars, membranes, pellets, drums, carbon foils, coated laminates, wire coverings, substrates for xerography, packaging, tapes, bottles, coatings, laminates, barrier products, membranes, molded articles, and combinations thereof.

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.
PCT/US 00/02624

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F220/44 B29C47/00 B29C45/00 B29C49/00 B29C51/00
B29D7/01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F B29C B29D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 492 909 A (STANDARD OIL CO OHIO) 1 July 1992 (1992-07-01) page 4, line 6 - line 16 examples	1-12, 18-20
X	US 4 039 734 A (HENDY BRIAN NORMAN) 2 August 1977 (1977-08-02) column 10, line 43 - column 11, line 52 column 14, line 1 - line 18	1-13, 15, 18-20
X	US 4 081 592 A (GIDDINGS BRANDFORD E ET AL) 28 March 1978 (1978-03-28) column 3, line 6 - line 16 examples	1-12, 14, 18-20

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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A document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 780 498 A (STANDARD OIL CO OHIO) 25 June 1997 (1997-06-25) examples claims	1-9
X	US 5 618 901 A (SMIERCIAK RICHARD C ET AL) 8 April 1997 (1997-04-08) cited in the application examples	1-9
X	US 5 602 222 A (SMIERCIAK RICHARD C ET AL) 11 February 1997 (1997-02-11) cited in the application column 1, line 34 - line 63 column 2, line 13 - line 16 examples	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/02624

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0492909	A	01-07-1992	US 5106925 A	21-04-1992
			AT 134660 T	15-03-1996
			CA 2057102 A	22-06-1992
			CN 1063289 A,B	05-08-1992
			CN 1106837 A	16-08-1995
			DE 69117472 D	04-04-1996
			DE 69117472 T	11-07-1996
			ES 2083536 T	16-04-1996
			HK 1007316 A	09-04-1999
			JP 5271352 A	19-10-1993
			MX 9102725 A	01-06-1992
			US 5286828 A	15-02-1994
US 4039734	A	02-08-1977	GB 1338561 A	28-11-1973
			GB 1197721 A	08-07-1970
			BE 695807 A	20-09-1967
			CH 501017 A	31-12-1970
			CH 533649 A	28-02-1973
			DE 1720942 A	12-08-1971
			DE 1745028 A	29-07-1971
			DK 130925 B	05-05-1975
			FR 1515628 A	12-06-1968
			FR 1566490 A	09-05-1969
			GB 1185305 A	25-03-1970
			LU 53266 A	23-05-1967
			NL 6704231 A,B	25-09-1967
			NL 6803178 A	09-09-1968
			SE 350269 B	23-10-1972
			AT 291604 B	15-06-1971
			BE 695809 A	20-09-1967
			CH 498169 A	31-10-1970
			CH 500240 A	15-12-1970
			DE 1694449 A	08-07-1971
			ES 338344 A	16-06-1968
			FR 1523483 A	19-09-1968
			GB 1186361 A	02-04-1970
			JP 52029392 A	05-03-1977
			LU 53226 A	22-05-1967
			NL 6704296 A,B	25-09-1967
			NL 6803336 A	11-09-1968
			SE 380536 B	10-11-1975
			BE 711836 A	09-09-1968
			GB 1185308 A	25-03-1970
			LU 55628 A	21-05-1968
			SE 354665 B	19-03-1973
			SE 354666 B	19-03-1973
			SE 372540 B	23-12-1974
			BE 711965 A	09-09-1968
			DE 1694497 A	07-10-1971
			FR 1559289 A	07-03-1969
			LU 55648 A	26-05-1968
US 4081592	A	28-03-1978	NONE	
EP 0780498	A	25-06-1997	AU 716405 B	24-02-2000
			AU 7532096 A	26-06-1997
			CA 2187414 A	19-06-1997
			TR 970523 A	21-07-1997

INTERNATIONAL SEARCH REPORT

information on patent family members

Inter. Appl. Application No.

PCT/US 00/02624

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5618901 A	08-04-1997	AU 709715 B	02-09-1999
		AU 4571796 A	05-09-1996
		CA 2170117 A	28-08-1996
		CN 1147823 A	16-04-1997
		EP 0728777 A	28-08-1996
		JP 9512587 T	16-12-1997
		TR 960857 A	21-10-1996
		WO 9626968 A	06-09-1996
		CA 2134823 A	11-05-1995
		CN 1107166 A	23-08-1995
		EP 0741150 A	06-11-1996
		US 5602222 A	11-02-1997
US 5602222 A	11-02-1997	CA 2134823 A	11-05-1995
		CN 1107166 A	23-08-1995
		EP 0741150 A	06-11-1996
		US 5618901 A	08-04-1997